Complex Octahedral Tilt Phases in the Ferroelectric Perovskite System $Li_xNa_{1-x}NbO_3$

Charlotte A. L. Dixon and Philip Lightfoot*

School of Chemistry and EaStCHEM, University of St Andrews, St Andrews,

KY16 9ST, UK

*E-mail pl@st-and.ac.uk

Supplementary information

In addition to the Figures and Tables herein and CIFs for refined models at selected compositions and temperatures (listed below), we deposit the following extra supplementary file:

Simultaneous MRT tilt systems.docx: output from the ISODISTORT program showing all 96 possible models arising from simultaneous presence of the R4+, M3+ and T4 (1/2,1/2,1/4) irreps, as referred to in the text.

CIF files for review and deposition:

Refined data and model	Filename (.cif)
1. LNN-3 at 20 °C, space group $P2_1ma$	LNN3_20C_phaseQ
2. $P4/mbm$ idealized model with T_4 mode at γ = 6/20 and 7/20 (Phase S''')	LNN3_P4mbm_6_20_7_20
3. LNN-3 at 500 °C, space group $Cmcm$	LNN3_550C_T1
4. LNN-3 at 600 °C, space group $P4/mbm$	LNN3_600C_T2
5. LNN-3 at 900 °C, space group $Pm\bar{3}m$	LNN3_900C_U
6. LNN-8 at 150 °C, space group $P2_1ma$	LNN8_150C_Q
7. $P4/mbm$ idealised model for phase S'' with T_4 mode at γ = 4/15	P4mbm_30ap_S''
8. Idealised model pertaining to the complex tilt system shown in Fig. S7, for LNN-8.	$P4mbm$_4_15
9. LNN-8 at 600 °C, space group $Cmcm$	LNN8_600C_T1
10. LNN-8 at 650 °C, space group $P4/mbm$	LNN8_650C_T2
11. LNN-8 at 900 °C, space group $Pm\bar{3}m$	LNN8_900C_U
12. LNN-12 at 150 °C, space group $P2_1ma$	LNN12_150C_Q
13. LNN-12 at 400 °C, space group $Pnma$	LNN12_400C_S'
14. LNN-12 at 650 °C, space group $Cmcm$	LNN12_650C_T1
15. LNN-12 at 700 °C, space group $P4/mbm$	LNN12_700C_T2
16. LNN-12 at 900 °C, space group $Pm\bar{3}m$	LNN12_900C_U

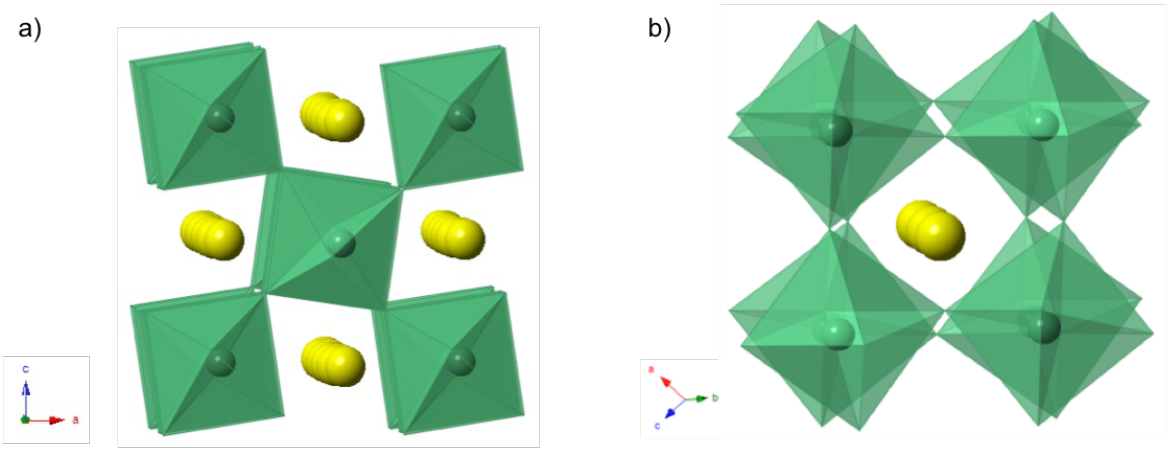

Figure S1: Crystal structure of phase Q (a) looking down the *b*-axis and highlighting the in-phase tilt mode, and phase N (b) highlighting the out of phase tilt along each of the crystallographic axes.

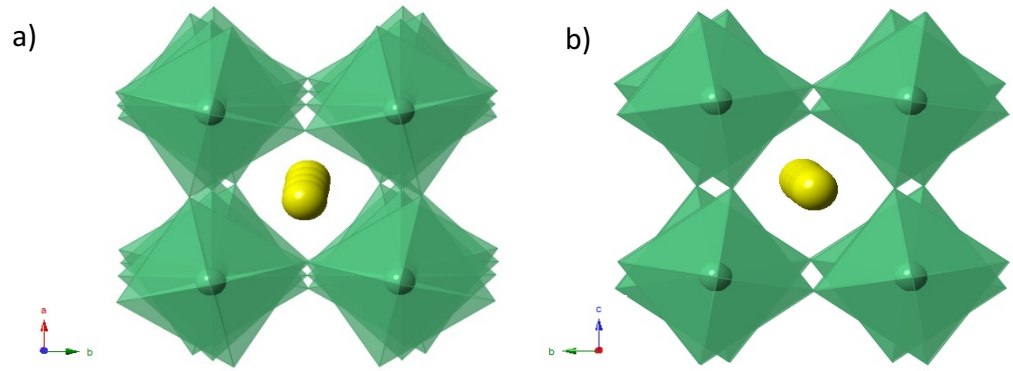

Figure S2: Representations of the two configurations of the T_4 (***k*** = (½, ½, ¼)) octahedral tilting mode as a) A0C0 and b) AACC.

Table S1: Crystallographic data for Phase S' in LNN-12 at 400 °C. a = 7.82835(15) Å, b = 7.8196(2) c = 15.6409(4) Å.

Atom	Wyckoff position	x	y	z	100 * U_{iso} (Å^2)
Na1*	4c	0.236(5)	0.25	0.873(3)	2.30(12)
Na2	4c	0.242(16)	0.25	0.122(2)	2.30(12)
Na3	4c	0.249(7)	0.25	0.376(3)	2.30(12)
Na4	4c	0.250(6)	0.25	0.376(3)	2.30(12)
Nb1	4a	0	0	0	0.70(3)
Nb2	8d	0.00010(8)	0.0005(7)	0.2506(8)	0.70(3)
O1	8d	0.0252(11)	0.0334(14)	0.8752(9)	1.57(3)
O2	8d	0.0235(12)	0.0182(11)	0.3749(9)	1.57(3)
O3	8d	0.2500(17)	-0.0359(10)	-0.0161(6)	1.57(3)
O4	8d	0.2483(12)	0.0151(9)	0.2690(7)	1.57(3)
O5	4c	0.039(2)	0.25	0.0144(10)	1.57(3)
O6	4c	-0.0076(16)	0.25	0.2345(12)	1.57(3)
O7	4c	-0.033(2)	0.25	0.5214(9)	1.57(3)
O8	4c	0.0290(19)	0.25	0.7260(8)	1.57(3)

*positions Na1-Na4 have fixed occupancy $Na_{0.88}Li_{0.12}$.

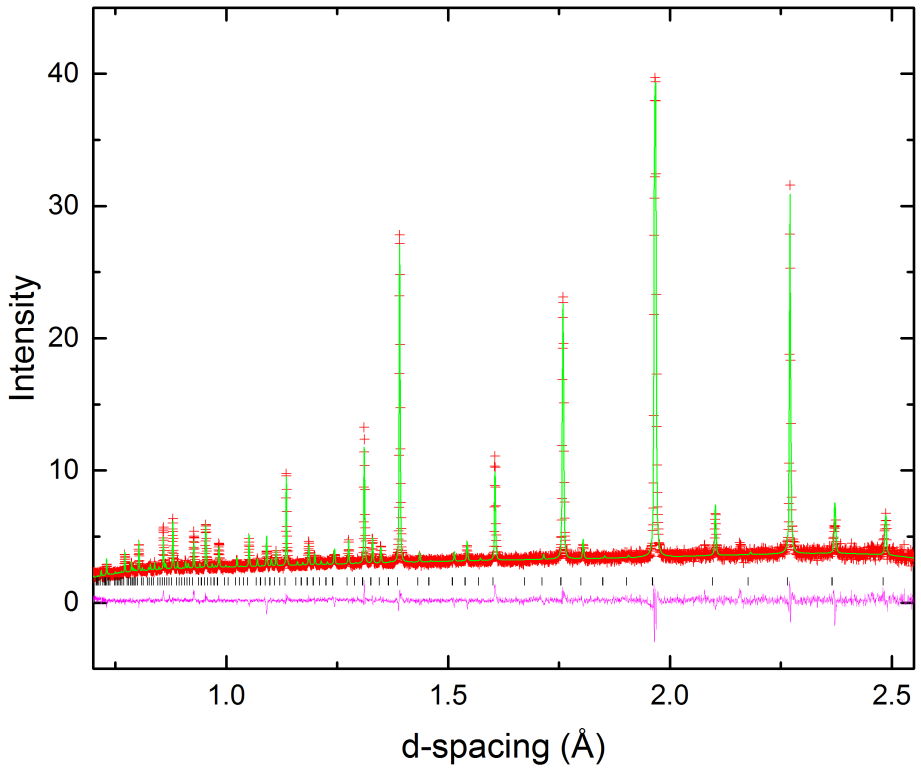

Figure S3: Rietveld refinement of T1, *Cmcm* phase of LNN-12 at 650 °C; χ^2 = 1.68, R_{wp} = 0.0454.

Table S2: Crystallographic data for LNN-12 at 650 °C modelled in the *Cmcm* (T1) space group; *a* = 7.86345(17) Å, *b* = 7.85644(17) Å, *c* = 7.786992(17) Å. U_{iso} values for all A-site cations (Na,Li) are constrained together.

Atom	Wyckoff position	*x*	*y*	*z*	100 * U_{iso} (Å^2)
Na1*	4c	0	0.005(3)	0.25	4.6(6)
Na2	4c	0	0.493(3)	0.25	3.7(5)
Nb	8d	0.25	0.25	0	1.16(3)
O1	8e	0.2832(6)	0	0	3.50(14)
O2	8f	0	0.2312(6)	0.0129(8)	2.25(15)
O3	8g	0.2653(8)	0.2635(10)	0.25	3.38(13)

*positions Na1 and Na2 have fixed occupancy $Na_{0.88}Li_{0.12}$.

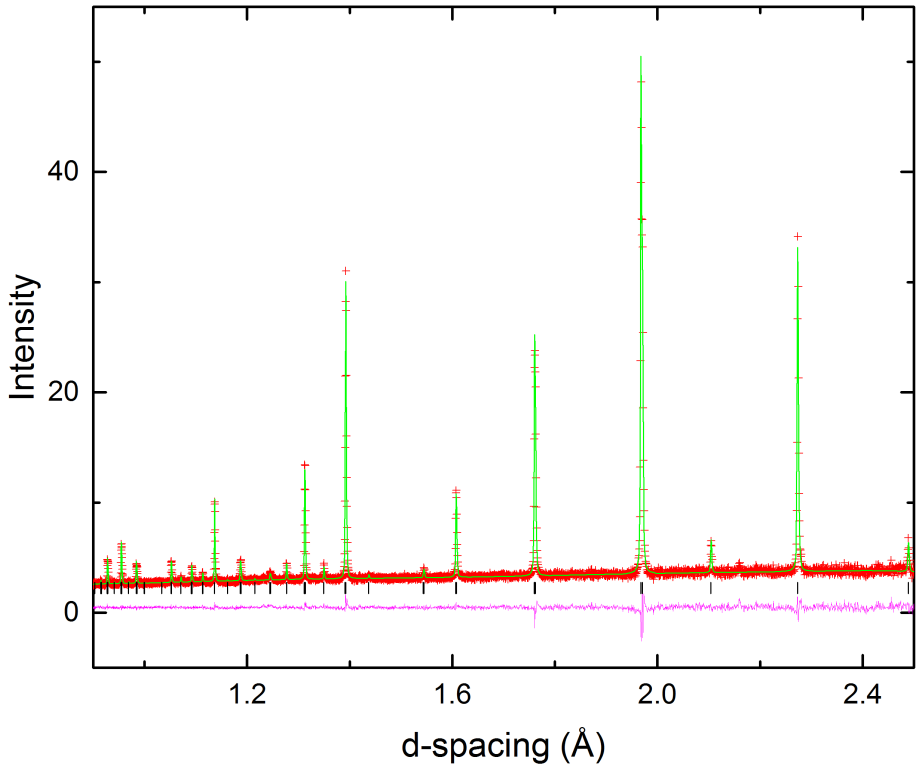

Figure S4: Fit to PND data at 700 °C on LNN-12 for the tetragonal phase, T2, with *P*4/*mbm* symmetry. χ^2 = 1.44, R_{wp} = 0.0316.

Table S3: Crystallographic data for LNN-12 at 700 °C modelled in the *P*4/*mbm* space group. *a* = 5.56482(8) Å, *c* = 3.94063(6) Å. U_{iso} values for all A-site cations (Na,Li) are constrained together.

Atom	Wyckoff position	*x*	*y*	*z*	100 * $U_{11/22}$ (Å^2)	100*U_{12} (Å^2)	100*U_{33} (Å^2)
Na*	2a	0	0.5	0.5	4.71(17)	-0.72(2)	3.1(3)
Nb	2c	0	0	0	1.23(6)	0	1.25(12)
O1	2b	0	0	0.5	7.0(2)	0	0.86(14)
O2	4g	0.27136(18)	0.22865(18)	0	2.34(8)	-0.158(9)	6.36(14)

*position Na has fixed occupancy $Na_{0.88}Li_{0.12}$.

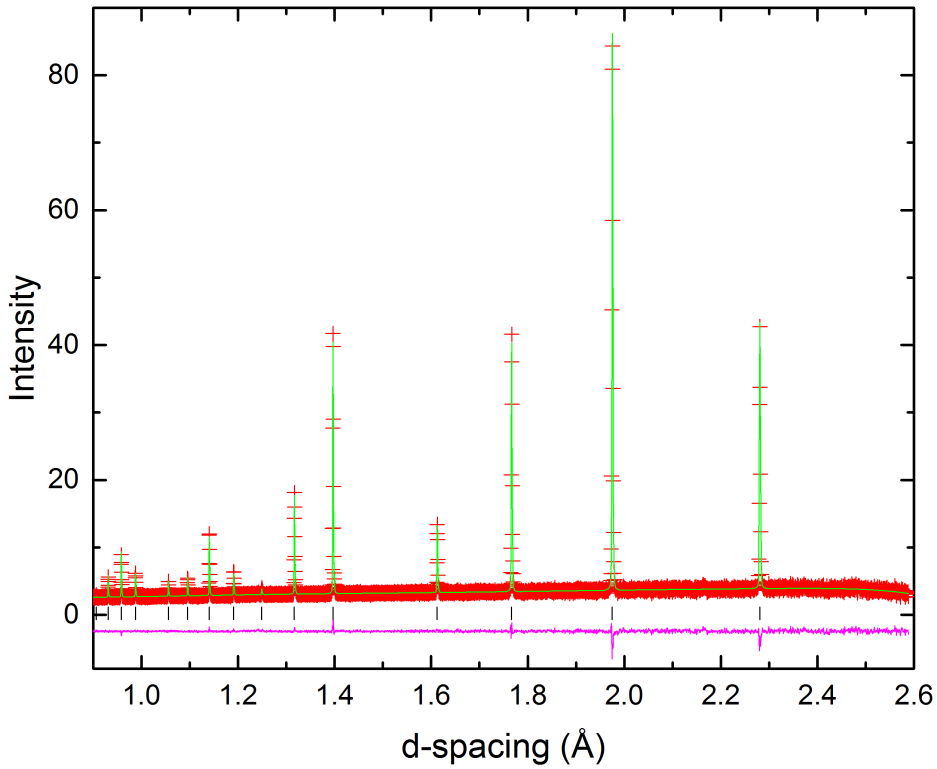

Figure S5: Fit to PND data at 900 °C on LNN-12 for the cubic phase, U, $Pm\bar{3}m$ symmetry. χ^2 = 1.30, R_{wp} = 0.0301.

Table S4: Crystallographic data for LNN-12 at 900 °C modelled in the $Pm\bar{3}m$ (U) space group. a = 3.95246(3) Å. U_{aniso} values for all A-site cations (Na,Li) are constrained together.

Atom	Wyckoff position	*x*	*y*	*z*	100 * U_{11} (Å^2)	100*$U_{22/33}$ (Å^2)
Na*	2a	0	0	0	6.07(5)	6.07(5)
Nb	2c	0.5	0.5	0.5	1.299(18)	1.299(18)
O	2b	0	0.5	0.5	0.95(3)	6.49(3)

*position Na has fixed occupancy $Na_{0.88}Li_{0.12}$.

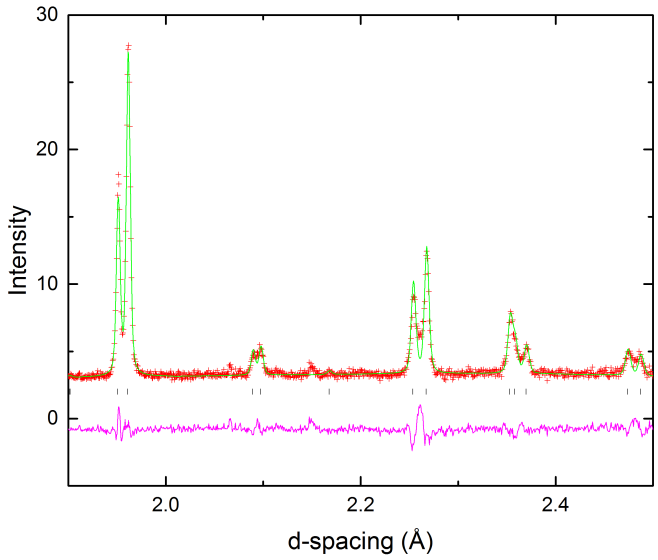

Figure S6: Rietveld refinement of LNN-8 at 300 °C showing that phase Q is the sole phase present at this temperature; χ^2 = 1.79, R_{wp} = 0.0402.

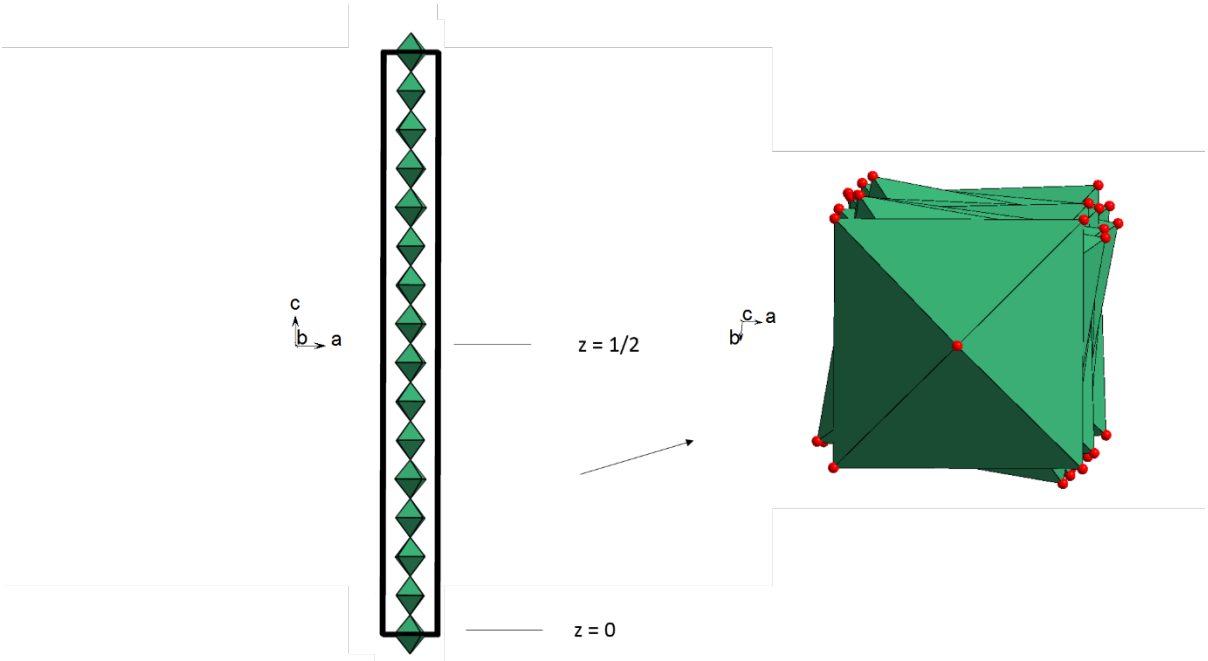

Figure S7: Complex octahedral tilt (T4 mode (1/2,1/2,4/15) for Phase S'' of LNN-8, space group *P*4/*mbm*. The left-hand plot show the 15-fold superlattice along *c*. The right-hand plot shows a plan view of the tilt system. Only octahedra between *z* = 0 and *z* = ½ are shown; the mirror plane at z = ½ completes the unit cell.

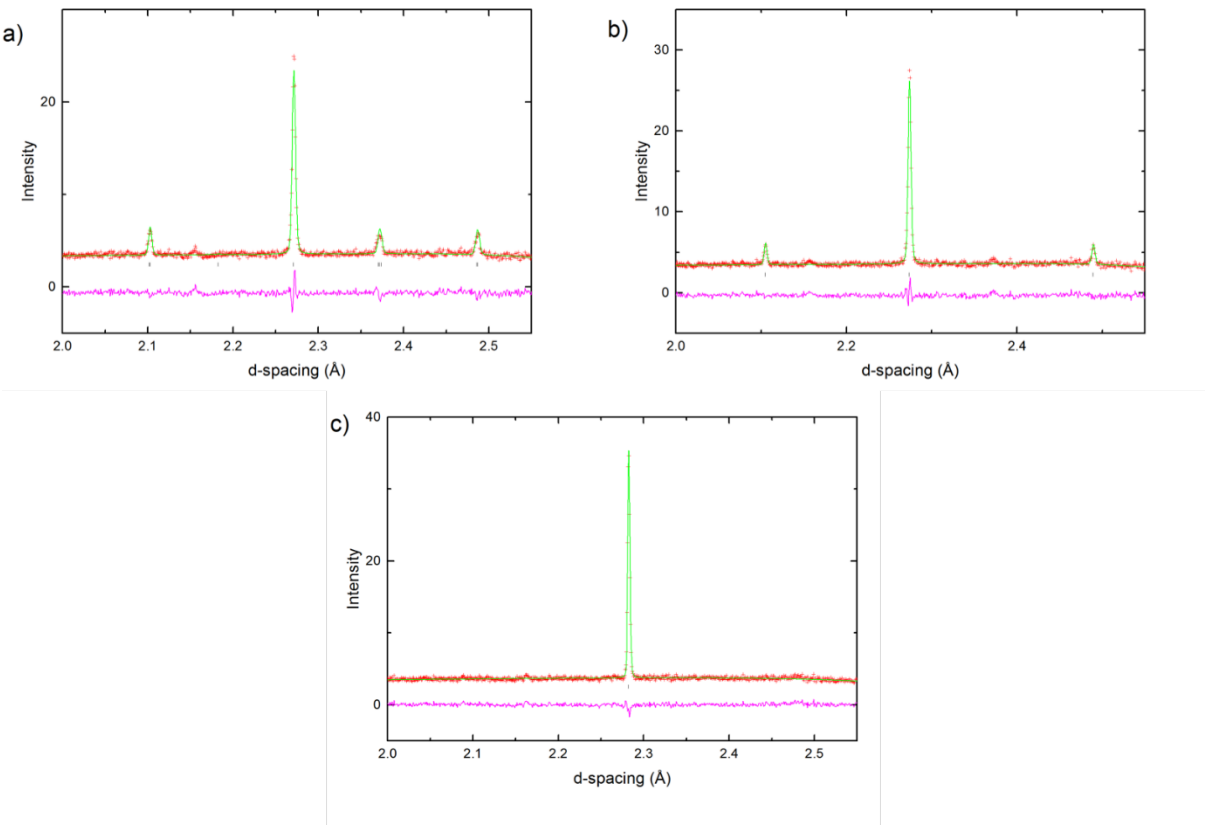

Figure S8: Rietveld plots of for LNN-8: phases T1 at 600 °C (a), T2 at 650 °C (b), and U at 900 °C (c).

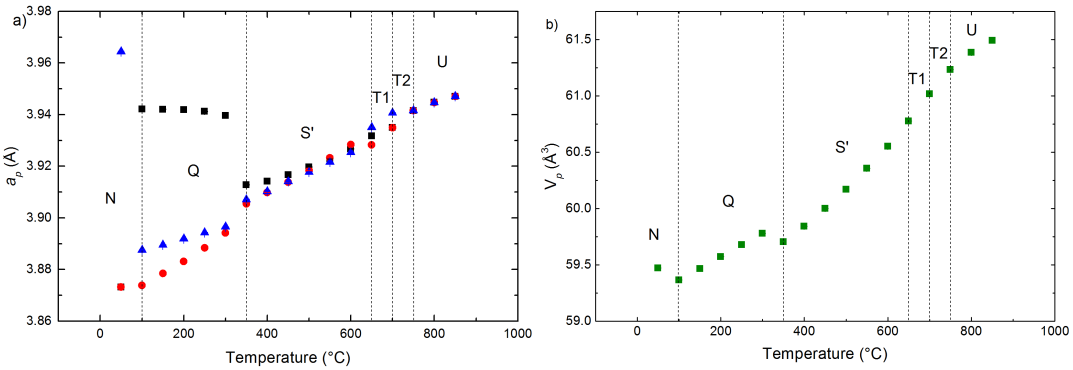

Figure S9 (a): Thermal evolution of normalised lattice parameters (a) and normalised unit cell volume (b) for a sample of LNN-12. The *a* lattice parameter is represented by black squares, *b* by red circles and *c* by blue triangles. For regions in which a phase co-existence is present only the majority phase is depicted.

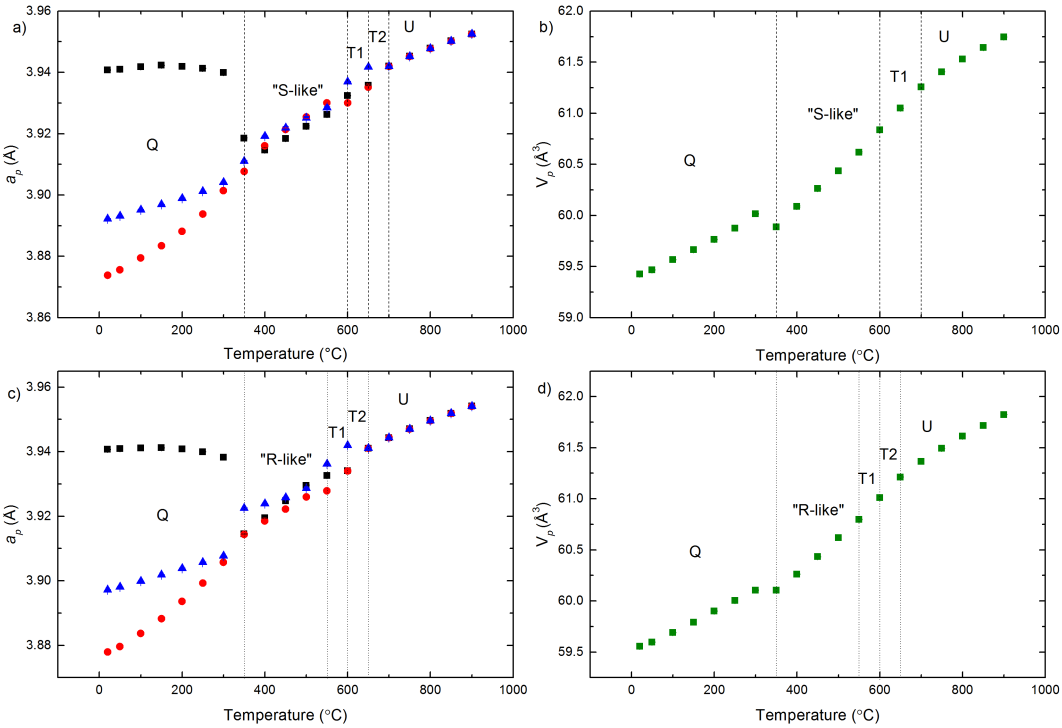

Figure S10: Thermal evolution of normalised lattice parameters and normalised unit cell volume obtained from PND data on a sample of LNN-8, (a and b) and LNN-3, (c and d). The *a* lattice parameter is represented by black squares, red circles denote *b* and blue triangles denote *c*. Lattice parameters from the majority phase only in regions of phase co-existence are shown.

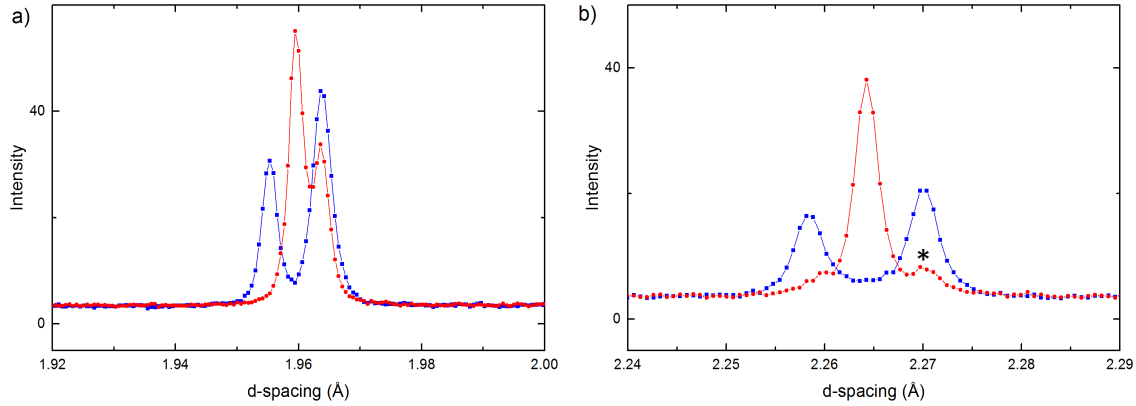

Figure S11: Raw PND data taken from bank 1 on LNN-3 at 300 °C (blue) and 350 °C (red) highlighting the 1st order nature of the phase transition, as evidenced by the change in the peak profile in (a), and the small residual amount of phase Q * (b).

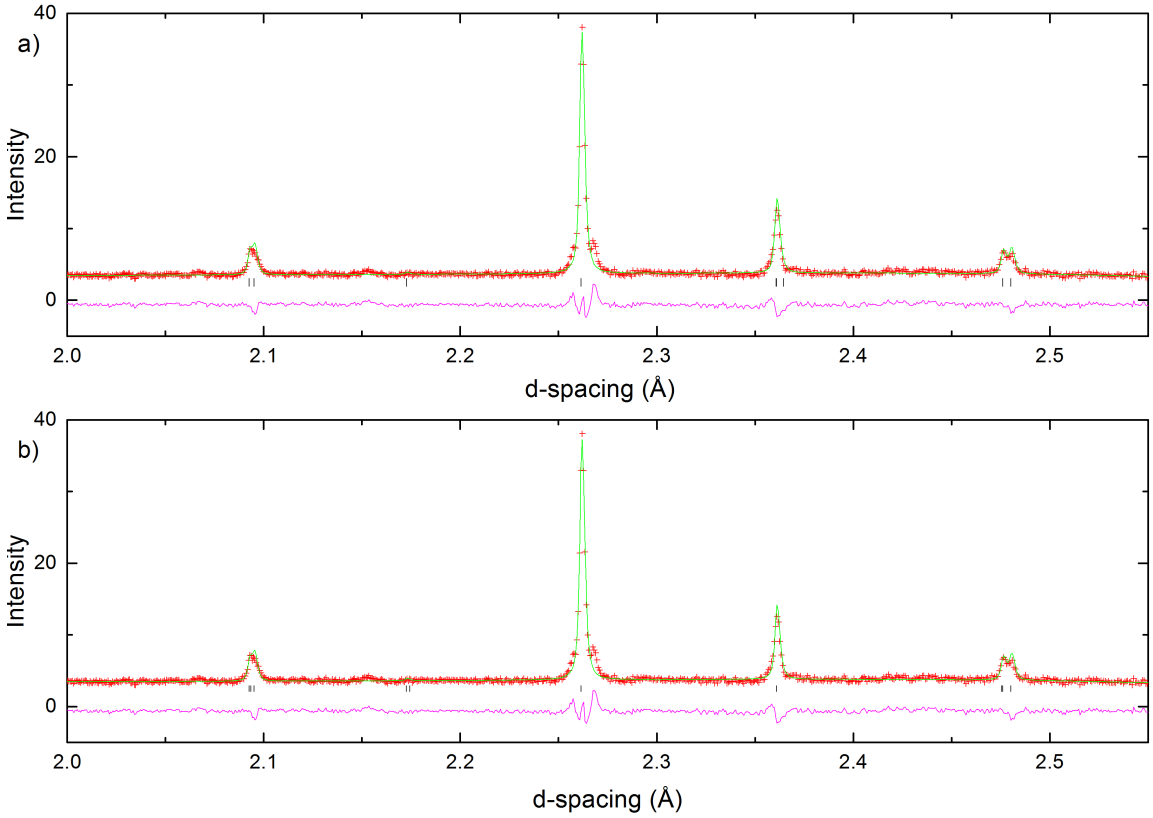

Figure S12: Results of Rietveld refinement on LNN-3 sample at 350 °C modelled using bank 1 data in (a) the *Cmcm* space group and (b) the $P4_2/nmc$ space group.

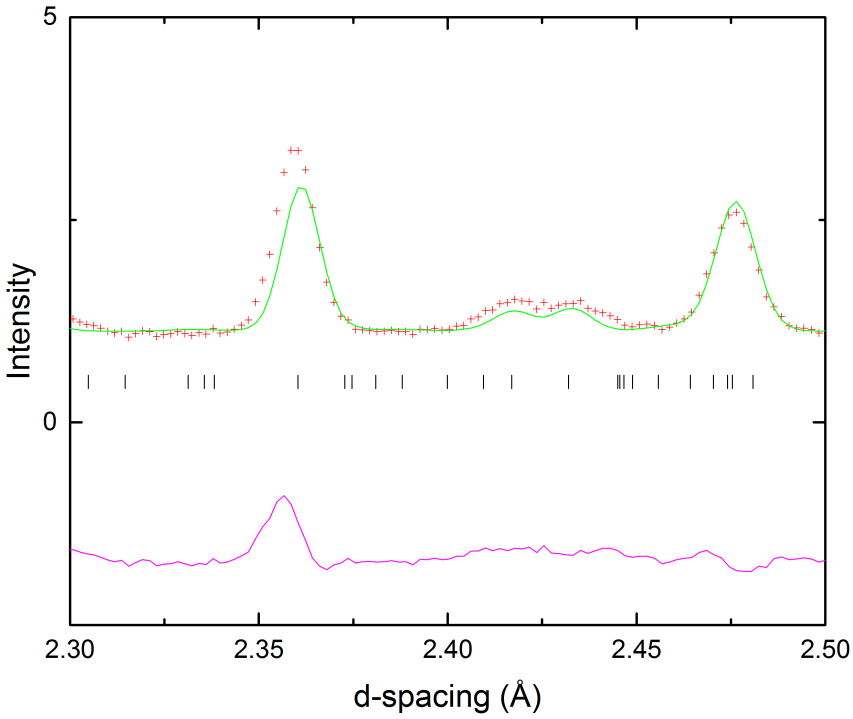

Figure S13: Modelling of the T_4 peaks (d ~ 2.40-2.45 Å) in LNN-3 at 400 °C in the *P*4/*mbm* spacegroup with a $\sqrt{2}\ a_p \times \sqrt{2}\ a_p \times 20\ a_p$ with T_4 modes with γ= 6/20 and 7/20. In this simple model the R_4^+, M_3^+ and T_4 modes all act along the c-axis.

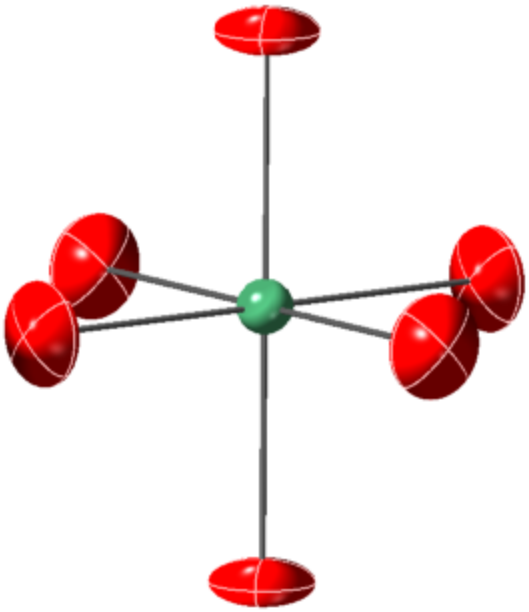

Figure S14: Thermal ellipsoids for cubic phase taken from Rietveld refinement of LNN-3 at 900 °C, highlighting anisotropic nature of the O atom ellipsoids.